One-step solvent-free synthesis of cyclic carbonates by oxidative carboxylation of styrenes over a recyclable Ti-containing catalyst

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ABSTRACT

A mesoporous titanium-silicate prepared by evaporation-induced self-assembly is an efficient heterogeneous catalyst for the one-step oxidative carboxylation of styrenes with *tert*-butyl hydroperoxide and carbon dioxide in the presence of tetrabutylammonium bromide as cocatalyst under mild solvent-free conditions (50–70 °C, 8 bar CO_2). The selectivity to cyclic carbonates reaches 69–70% at 92–98.5% substrate conversion. The catalyst can be easily recovered by filtration and reused several times without a significant deterioration of the catalytic performance. The volume yield of SC as high as 1.1 kg/L could be achieved after seven reuses.

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1. Introduction

The transformation of carbon dioxide into useful organic chemicals is becoming an increasingly popular research topic [1–11]. CO_2 is not only one of the greenhouse gases and a waste compound from chemical industry, power plants and transportation sector [12,13], but also an easily available, inexpensive, non-toxic, and non-flammable carbon feedstock [1–11]. However, CO_2 is not widely used in the industry, obviously because of its low reactivity. Substantial energy input, highly active catalysts and optimum reaction conditions are necessary for successful conversion of thermodynamically stable CO_2 molecules [1–11,14].

The synthesis of cyclic carbonates by means of CO_2 cycloaddition to epoxides is one of promising technologies for chemical fixation and utilization of CO_2 [15–25]. Cyclic carbonates such as ethylene carbonate, propylene carbonate and styrene carbonate (SC) are widely used as aprotic polar solvents, precursors for polycarbonate materials, electrolytes in lithium secondary batteries, antifoam agents for antifreeze, plasticizers, and starting materials for various chemical transformations [26–29].

The direct synthesis of cyclic carbonates from olefins and CO_2 through oxidative carboxylation (Scheme 1), that formally involves a combination of alkene epoxidation and cycloaddition of CO_2 to the epoxide formed, could be a more economically viable process because it operates with the low-cost and easily available feedstock, alkenes, and does not require separation of epoxide after the first step. Although the oxidative carboxylation of olefins has been known for a long time, since 1962 [30], only a few reports have been published so far [31–46], in contrast to the extensive studies on the cycloaddition of CO_2 to epoxide [15–25].

Aresta et al. reported direct synthesis of SC from styrene, CO_2 and O_2 using a homogeneous rhodium complex or metal oxides (Nb_2O_5, MgO, Fe_2O_3, V_2O_5, etc.) as catalysts under rather harsh reaction conditions (120 °C, 5 bar O_2, 45 bar CO_2) [31,32]. The reaction gave low SC yields (10–20%) and large amounts of byproducts such as benzaldehyde and benzoic acid.

Bai and Jing found that addition of a quaternary onium salt as cocatalyst to a ruthenium complex enabled a 76% SC yield at relatively mild reaction conditions (5 bar O_2, 11 bar CO_2, 30 °C, 48 h, CH_2Cl_2 as solvent) [33]. Use of *tert*-butyl hydroperoxide (TBHP) as oxidant and quaternary ammonium halides or imidazolium salts as catalysts gave SC in a yield of 38% but required high CO_2 pressure (150 bar) [34,35]. The reaction can be also accomplished at milder conditions (room temperature, 8 bar CO_2) [36]. A catalytic system consisting of silica or $Fe(OH)_3$-supported gold catalysts, zinc
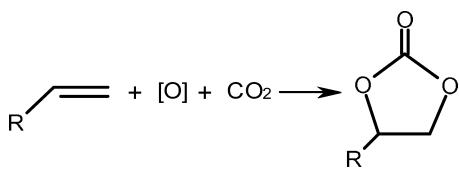
Scheme 1. Synthesis of cyclic carbonates through oxidative carboxylation of alkenes.

bromide and tetrabutylammonium bromide (TBABr) enabled production of SC in a 42–43% yield from styrene, organic peroxide and CO_2 (80 °C, 10–40 bar CO_2) [37,38]. While the Au-catalyst was responsible for epoxidation of styrene, the combination of $ZnBr_2$ and TBABr catalyzed cycloaddition of CO_2 to the epoxide formed. Eghbali and Li reported a highly selective conversion of alkenes and CO_2 into cyclic carbonates with yields up to 95% in water in the presence of catalytic amounts of N-bromosuccinimide or bromide using aqueous H_2O_2 as oxidant and 1,8-diazabicyclo[5.4.0]undecenc-7-ene as a base at 60 °C and 21 bar CO_2 [39]. Finally, sodium phosphotungstate $Na_2H_5P(W_2O_7)_6$ in combination with 30% H_2O_2, TBABr and $NaHCO_3$ produced carbonate yields up to 83% under 24 bar CO_2 and 50 °C [40].

Good carbonate yields can be obtained using one-pot multistep protocols that involve a consecutive loading of the reactor with an epoxidation catalyst and oxidant, and then with CO_2 and a cycloaddition catalyst [41–44]. For example, molybdenyl acetylacetonate in combination with a quaternary ammonium salt and TBHP enabled production of cyclic carbonates in 68–84% yields under 30 bar CO_2 and 100–140 °C [41]. Ono et al. reported synthesis of SC with a 83% yield from styrene and CO_2 using a catalytic system consisting of methyltrioxorhenium as epoxidation catalyst, urea-H_2O_2 as oxidant, and Zn[emim]$_2$Br$_4$ (emim = 1-ethyl-3-methylimidazolium) as catalyst for epoxide-CO_2 coupling in ionic liquid [BMIm]BF$_4$ (BMIm = 1-butyl-3-methylimidazolium) as solvent (110 °C, 30 bar CO_2) [42]. Recently, Girard et al. demonstrated catalytic activity of imidazolium-based ionic liquids in oxidative carboxylation [43]. In the presence of 10 mol% of BMImBr, SC was produced in 36 and 62% yields through one- and two-step protocols, respectively, using TBHP as oxidant in the absence of any additional solvent (5 bar CO_2, 150 °C) [43]. CO_2 can act not only as reagent but also as a solvent. A gold catalyst supported on a basic resin with anhydrous TBHP as oxidant and CO_2 (40 bar) as solvent produced SC in a yield of 51% [44]. The epoxidation and cycloaddition steps were conducted at 80 and 150 °C, respectively. On the other hand, a simpler single-step protocol gave only 1.5% of SC at 40 bar CO_2 and 100 °C [44].

Titanosilicate molecular sieves are well-known for their remarkable catalytic activity in a range of selective oxidation reactions with H_2O_2 or TBHP as oxidant [47–54], and specifically, in epoxidation of alkenes [55–62]. Srivastava et al., first reported an application of microporous titanium-silicalite-1 (TS-1) and mesoporous Ti-MCM-41 in the direct synthesis of cyclic carbonates from olefin, oxidant (H_2O_2 and TBHP, respectively) and CO_2 [45]. With Ti-MCM-41/TBHP and N,N-dimethylaminopyridine as cocatalyst, they achieved SC yield of 33% at 44% styrene conversion in two steps in a single reactor under 6.9 bar CO_2 and 120 °C with acetonitrile (MeCN) as solvent. However, the question of the catalyst recycling and reusability was not addressed [45].

Recently, a bifunctional material prepared by grafting quaternary ammonium bromide (OEt)$_3$Si(CH$_2$)$_3$-N$^+$Bu$_3$Br$^-$) on a delaminated titanosilicate Del-Ti-MWW was employed for the one-pot propylene oxidative carboxylation with 69% H_2O_2 and CO_2 [46]. A carbonate yield of 48% was attained (MeCN as solvent, 40–140 °C, 7 h, 20 bar CO_2). However, both the catalytic activity and product yield decreased dramatically in the second run, most likely, because

of pore blocking by heavy byproducts [46]. Therefore, the search for highly efficient and easily recyclable catalysts for the direct synthesis of cyclic carbonates from olefins and CO_2 still remains a great challenge.

In the present work, we first explored the catalytic performance of mesoporous titanium-silicates Ti-MMM-E and Ti-MMM-2 prepared by two different methodologies, evaporation-induced self-assembly (EISA) [63] and hydrothermal synthesis [64], respectively, in oxidative carboxylation of styrenes with environmentally friendly oxidants, H_2O_2 and TBHP. For the sake of comparison, we also evaluated catalytic properties of a Ti-based metal-organic framework (MOF), MIL-125. Special attention was drawn to the crucial issues of the catalyst stability and recyclability as well as employment of solvent-free conditions.

2. Experimental

2.1. Materials

Commercially available carbon dioxide (98.8%) was used without purification. Cetyltrimethylammonium bromide (CTAB, 99+ %), tetraethylorthosilicate (TEOS, 98+ %), tetraethoxy titanium(IV) (TEOT, 97+ %), acetylacetone (99%), TBHP (5.5 M in decane) and TBABr (99%) were purchased from Aldrich. TBHP (70% in water) was purchased from Merck. Hydrogen peroxide (ca. 35% in water) was determined by iodometric titration prior to use. Acetonitrile (Panreac, HPLC grade) was dried and stored over activated 4 Å molecular sieves. Column chromatography was performed using silica gel 70–230 mesh (63–200 μm), pore size 60 Å (Sigma–Aldrich). Other reactants were obtained commercially and used without additional purification. Deionized water (EASY pure, RF, Barnsted) was used for the preparation of catalysts.

2.2. Catalyst preparation and characterization

The Ti-MMM-E catalyst was prepared through EISA in ethanol/H_2O/HCl solution using TEOT modified with acetylacetone (1:1 mol/mol) as titanium precursor, TEOS as silica precursor, and CTAB as template according to the published protocol [63]. The mesoporous mesophase material Ti-MMM-2 was prepared by hydrothermal synthesis under moderately acidic conditions (pH 3.0) following a two-step procedure described previously [54,64], using sodium silicate as Si source and CTAB as template. The catalysts were calcined at 550 °C for 5 h in air prior to use in catalytic tests or before physical measurements. After calcination, the solids were grounded to give a fine powder.

Ti-MIL-125 was synthesized by a solvothermal method using terephthalic acid and titanium isopropoxide in a solvent mixture of N,N'-dimethylformamide and methanol as reported elsewhere [65,66]. The MOF structure was corroborated by XRD.

2.3. General procedure for oxidative carboxylation of styrene

Styrene (0.2 mmol), TBABr (0.02 mmol), TBHP (0.3 mmol) or H_2O_2 (0.3 mmol), Ti-catalyst (40 mg of Ti-MMM catalysts, i.e., 0.012 mmol Ti for Ti-MMM-E and 0.020 mmol Ti for Ti-MMM-2; or 5 mg of Ti-MIL-125, i.e., 0.020 mmol Ti), biphenyl (internal standard for GC) and MeCN (2 mL) were added into a 50 mL high pressure/high temperature stainless steel Parr-4792 reactor with PTFE insert. CO_2 was introduced into the reactor, and the pressure was adjusted to 8 bar. The mixture was stirred continuously while the pressure (8 bar) and temperature (50 °C) were kept constant during the reaction. After specified reaction time (24 or 48 h), the reactor was cooled down by ice water and depressed slowly before opening. The reaction products were identified by GC–MS and quantified by GC. Each experiment was reproduced at least 2 times.

After the catalytic run, catalyst was separated by filtration and washed with solvent, dried in air at room temperature overnight, calcined in air at 350 °C for 2 h and at 550 °C for 4 h, and then reused. The catalyst was characterized by DR UV–vis spectroscopy, N_2 adsorption measurements and elemental analysis before and after reuse; titanium content in the filtrate that remained after separation of the catalyst was determined by ICP-AES.

Styrene carbonate was isolated from the reaction mixture as described below. The reaction was scaled up: styrene (9.6 mmol), TBABr (0.96 mmol), TBHP (14.4 mmol), Ti-MMM-E (600 mg, 0.186 mmol Ti), CO_2 (8 bar). After 48 h at 70 °C, the reactor was cooled down by ice water and depressed slowly before opening. The reaction mixture was diluted with 10 mL of CH_2Cl_2, and the Ti-MMM-E catalyst was filtered off and washed several times with CH_2Cl_2 (total volume 30 mL). The organic solution was thoroughly washed with water (30 mL × 4) to remove TBABr (GC control) and dried over $MgSO_4$. The volatile components were removed under vacuum, and the residue was crystallized from diethyl ether–hexane. The resulting white solid (styrene carbonate, 0.4 g) was filtered off, and the filtrate was concentrated under vacuum and subjected to column chromatography with ethyl acetate–hexane (1: 20) as the eluent. The total isolated yield of styrene carbonate was 0.85 g (54%). The melting point of thus obtained SC was 49–50 °C in accordance with the literature data [67,68].

2.4. Instrumentation

GC analyses were performed using a gas chromatograph Tsvet-500 equipped with a flame ionization detector and a quartz capillary column (30 m × 0.25 mm) filled with Agilent DB-5MS. GC–MS analyses of organic products were carried out using Agilent 6890/MSD 5973 system (carrier gas He, 30 m × 0.25 mm × 0.25 μm capillary column HP-5). Nitrogen adsorption was carried out at 77 K using an Autosorb-6B-Kr instrument (Quantachrome Instruments). Before measurements, samples were degassed by evacuation at 300 °C for 3 h. Specific BET surface areas (A_{BET}) were evaluated using adsorption data over a relative pressure range of 0.05–0.15. Mesopore volume was determined from the quantity of nitrogen adsorbed at the relative pressure of 0.990. Modal pore diameter was evaluated as the mode of pore volume size distribution, calculated by NLDFT method (kernel: N_2/77 K on silica cylinder pore for adsorption branch). CO_2 adsorption was carried out at 273 K using an ASAP-2020 instrument (Micromeritics). XRD measurements were performed with a high-precision X-ray diffractometer mounted on beamline No. 2 of the VEPP-3 storage ring at the Siberian synchrotron radiation centre (SSRC). Particle size was estimated by SEM (JEOL JSM-6460 LV instrument). The state of titanium in the catalysts was probed by DR UV–vis spectroscopy under ambient conditions using a Shimadzu UV–vis 2501PC spectrophotometer. Scanning electron microscopy images were acquired by means of a JEOL JSM-6460 LV microscope. Titanium content in the solids and in the filtrate after separation of catalyst was determined by ICP-AES using a Thermo Scientific iCAP-6500 instrument.

3. Results and discussion

3.1. Catalyst characterization

The synthesis and characterization of the mesoporous titanium-silicates Ti-MMM-2 [64] and Ti-MMM-E [63] have been reported earlier. Briefly, Ti-MMM-2 has a well-ordered structure of 2D hexagonally packed mesopores-channels (ca. 3 nm) [64], while Ti-MMM-E represents a mesophase with a long-range structural ordering of cylindrical mesopores of a uniform pore size (3.5 nm)

[63]. Low-angle XRD patterns of the titanium-silicates are given in Fig. S1 in Supporting information (SI). According to our previous studies, both materials possess good hydrothermal stability [63,64]. SEM images (Fig. S2 in SI) show that Ti-MMM-E has relatively sharp particles with a size of 100–500 μm.

The titanium-oxo-hydroxo-cluster-based metal-organic framework Ti-MIL-125 was synthesized by a solvothermal method using terephthalic acid and titanium(IV) isopropoxide [65]. The structure of MIL-125 was confirmed by XRD (Fig. S1 in SI). This MOF is built up from cyclic octamers constructed from octahedral titanium units connected through 1,4-benzenedicarboxylate linkers and has two types of cages (12.5 and 6 Å in diameter) accessible through triangular windows of 5–7 Å [65].

The physicochemical properties of the catalyst samples used in this work are presented in Table 1. All the materials possess high surface areas and pore volumes. The titanium content in MIL-125 is an order of magnitude higher than in the titanium-silicates.

The nature of Ti species in titanium-containing catalysts has a strong impact on their catalytic performance [47–54,69–72]. Taking this into account, it is significant to note that the catalysts used in this work differed in the state of titanium. DR UV–vis spectroscopy allows one to distinguish between site-isolated and di(oligo) meric Ti centers [49,52–54,69–72]. DR UV–vis spectra of the catalysts are shown in Fig. S3 in SI. Ti-MMM-E reveals a broad absorption in the range of 230–260 nm, characteristic of Ti(IV) di(oligo) nuclear species well-dispersed within silica matrix [53,54,69,71,72]. On the other hand, the spectrum of Ti-MMM-2 shows a narrow band with a maximum at 216 nm, characteristic of site-isolated titanium [49,52–54,69,70,72]. The spectrum of Ti-MIL-125 has two absorptions maxima centered at ca. 240 and 290 nm that can be assigned to titanium oxo-hydroxo clusters [66].

3.2. Styrene oxidative carboxylation

The catalytic performance of the Ti-containing catalysts in the oxidative carboxylation of styrene was first evaluated in MeCN solution using 8 bar CO_2 and two types of oxidants-TBHP and H_2O_2 (Scheme 2). The results of the catalytic tests along with blank experiments are summarized in Table 2.

As it was mentioned in Section 1, quaternary ammonium salts promote the formation of cyclic carbonates [34–36,73]. Indeed, oxidative carboxylation of styrene in the presence of TBABr resulted in the formation of SC with 28% selectivity at 49% substrate conversion after 48 h at 50 °C (Table 2, entry 1). The main side products were benzaldehyde (BA, 42%) and styrene oxide (SO, 28%). In the presence of Ti-MMM-E (Table 2, entry 2), styrene conversion was lower (35%) while the selectivity of BA was higher (62%). On the other hand, use of TBABr in combination with Ti-MMM-E enabled 51% selectivity of SC at 71% styrene conversion under the same reaction conditions (Table 2, entry 3). Hence, we can speak about a synergistic effect of the titanium-silicate and quaternary ammonium salt in the title reaction. Again, the main by-products were BA and SO. Neither phenylacetaldehyde nor phenylacetic acid were detected in the reaction mixture by GC–MS.

Note that the oxidative C=C cleavage producing BA is a typical side reaction for styrene epoxidation, specifically, with hydroperoxides in the presence of Ti,Si-based catalysts [74–78]. Table 3 presents the results of transformations of styrene in the presence of TBHP over Ti-MMM-E and/or TBABr. One can see that the presence of TBABr favors the formation of BA from styrene (entries 2 and 3, Table 3). On the other hand, as we already mentioned above, TBABr is also necessary for the formation of carbonate (compare entries 2 and 3 in Table 2).

Previously, it was shown both TS-1 and Ti-MCM-41 in combination with N,N-dimethylaminopyridine as cocatalyst, in contrast to TiO_2 (anatase), are active catalysts for CO_2 cycloaddition to organic

Table 1
Physicochemical properties of Ti-containing catalysts.

Catalyst	Ti (wt%)	A_{BET}[a] (m²/g)	V[b] (cm³/g)	D[c] (nm)	DRS-UV max. (nm)
Ti-MMM-E	1.46	1020	0.67	3.5	230
	1.45[d]	930[d]	0.57[d]	3.4[d]	275[d]
Ti-MMM-2	2.4	1130	0.69	3.1	216
Ti-MIL-125	20.0	1870	0.76[e]	0.6–1.25 Cages; 0.5–0.7 windows	240, 290

[a] BET surface area.
[b] Mesopore volume.
[c] Means pore diameter.
[d] After catalyst reuse (reaction conditions as in Table 3, entry 4, 24 h).
[e] Micropore volume.

Table 2
Styrene oxidative carboxylation over Ti-containing catalysts.

Entry	Catalyst	Oxidant	Time (h)	Styrene conversion (%)	Product selectivity[a] (%)		
					BA	SO	SC
1	TBABr	TBHP	48	49	42	28	28
2	Ti-MMM-E	TBHP	48	35	62	27	11
3	Ti-MMM-E + TBABr	TBHP	24	44	46	30	22
			48	71	25	23	51
4	Ti-MMM-E + TBABr	TBHP	5+24[b]	43	28	50	15
5	TBABr	H_2O_2	48	9	62	23	15
6	Ti-MMM-E	H_2O_2	48	28	65	11[c]	4
7	Ti-MMM-E + TBABr	H_2O_2	24	33	9	64[c]	18
			48	44	5	25[c]	34
8	Ti-MMM-2 + TBABr	TBHP	48	35	40	26	34
9	Ti-MMM-2 + TBABr	H_2O_2	48	7	33	50	17
10	Ti-MIL-125 + TBABr	TBHP	48	36	39	50	8
11	Ti-MIL-125 + TBABr	H_2O_2	48	16	19	68	13

Reaction conditions: styrene 0.2 mmol, TBHP (5.5 M solution in decane) or H_2O_2 (35% in water) 0.3 mmol, TBABr 0.02 mmol, Ti,Si-catalyst 40 mg or Ti-MIL-125 5 mg, P(CO₂) 8 bar, MeCN 2 mL, 50 °C.

[a] GC yield based on substrate consumed.
[b] One-pot two-step process: 5 h for oxidation with TBHP over T-MMM-E + 24 h for CO₂ subsequent cycloaddition reaction in the presence of Ti-MMM-E and TBABr. After the first 5 h, styrene conversion was 39%, BA yield—10%, SO yield—29%.
[c] 1-Phenyl-1,2-ethanediol was also formed.
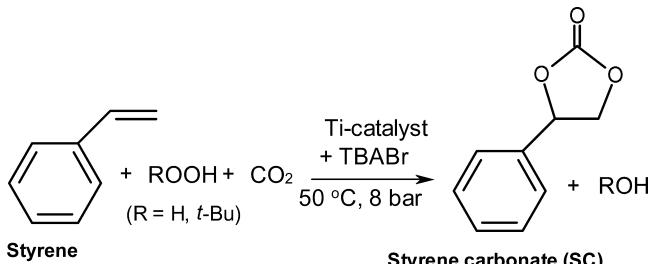
Scheme 2. Oxidative carboxylation of styrene over Ti-catalysts.

epoxides [45]. In agreement with these results, Ti-MMM-E turned out to be an active catalyst for CO₂ cycloaddition to styrene oxide: in the presence of TBABr as cocatalyst, SC formed with 62% selectivity at 45% SO conversion after 24 h at 50 °C. It is noteworthy that a one-pot two-step procedure, where styrene epoxidation with TBHP over Ti-MMM-E was followed by CO₂ cycloaddition in the presence of Ti-MMM-E and TBABr cocatalyst, led to a somewhat lower SC selectivity relative to the one-step process (Table 2, compare entries 3 and 4). One might explain this difference in terms of a kinetic competition between the transformation of SO to BA and the addition of CO₂ to SO. It is well-known that Lewis acid sites [79], and specifically Ti-centers [75,80], are able to promote conversion of SO to BA. Indeed, we found that SO partially transformed to BA in the presence of TBHP and Ti-MMM-E. However, when TBABr was also present, practically no conversion of SO was observed, probably, because bromide ions occupied the Lewis acid sites, which are necessary for SO transformation to BA.

With aqueous H_2O_2 instead of TBHP, both the substrate conversion and carbonate selectivity decreased (Table 2, compare entries 7 and 3). In the absence of the Ti-catalyst, the TBABr/H_2O_2 system showed much lower styrene conversion (9% after 48 h versus 44% in the presence of Ti-MMM-E) and carbonate selectivity (15 versus 34%; Table 2, entries 5 and 7).

To assess the influence of the titanium state on the catalytic performance, we carried out the oxidative carboxylation of styrene using Ti-MMM-2 as a representative mesoporous titanium-silicate catalyst containing mostly site-isolated Ti centers. Ti-MMM-2 appeared to be less active and selective than Ti-MMM-E with both oxidants (Table 2, compare entries 8 and 9 with entries 3 and 7, respectively). Since the textural properties of these catalysts are similar (see Table 1), we may suggest that di(oligo) meric titanium species are more preferable active centers for the title reaction than isolated Ti atoms, although the latter exhibit high activity and selectivity in epoxidation of alkenes with hydroperoxides (both TBHP and H_2O_2) [47–54]. This prompted us to evaluate the catalytic performance of the metal-organic framework Ti-MIL-125, the structure of which consists of titanium oxo-hydroxo clusters. Recently, Kim et al. reported that Ti-MIL-125 adsorbs large amounts of CO₂ and is active in cycloaddition of CO₂ to epichlorohydrine [81]. We compared the capability of Ti-MIL-125 and Ti-MMM-E of adsorbing carbon dioxide under the same conditions. Fig. S4 in SI shows that Ti-MIL-125 takes more CO₂ than Ti-MMM-E (175 versus 80 mg per g of the catalyst). However, the catalytic activity and selectivity of Ti-MIL-125 in styrene oxidative carboxylation with both TBHP and H_2O_2 (Table 2, entries 10 and 11) were inferior relative to Ti-MMM-E. We may suppose that molecules of styrene, SC and TBABr are too large to penetrate easily into the micropores of Ti-MIL-125, and the reaction probably takes place mainly on the

Table 3
Styrene oxidation in the presence of TBHP over Ti-MMM-E and/or TBABr.

Entry	Substrate	Catalyst	Substrate conversion (%)	Product selectivity[a] (%)	
				BA	SO
1	Styrene	Ti-MMM-E	39	26	74
2	Styrene	TBABr	23	64	32
3	Styrene	Ti-MMM-E + TBABr	35	61	39

Reaction conditions: styrene 0.1 mmol, TBHP (5.5 M solution in decane) 0.15 mmol, TBABr (if any) 0.01 mmol, Ti-MMM-E (if any) 20 mg (0.006 mmol Ti), MeCN 1 mL, 50 °C, 5 h.

[a] GC yield based on substrate consumed.
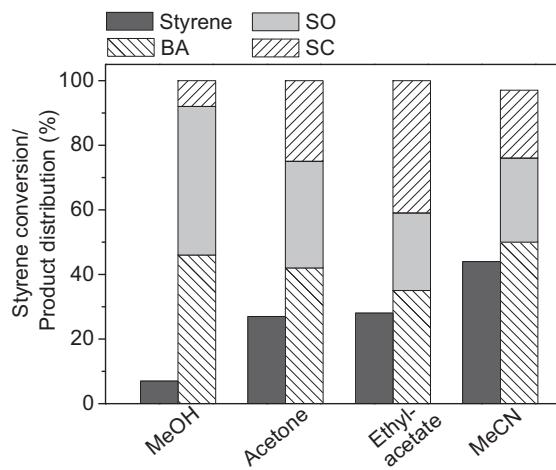
Fig. 1. Effect of the solvent nature on styrene oxidative carboxylation with TBHP and CO_2 over Ti-MMM-E. Reaction conditions as in Table 2, entry 3, 24 h.

Fig. 2. Effect of the reaction temperature on styrene oxidative carboxylation with TBHP and CO_2 over Ti-MMM-E. Reaction conditions as in Table 2, entry 3, 24 h.

Fig. 3. Effect of concentration on styrene oxidative carboxylation with TBHP and CO_2 over Ti-MMM-E. Reaction conditions: styrene/TBHP/TBABr/Ti molar ratio = 0.1/0.15/0.01/0.006, MeCN, $P(CO_2)$ 8 bar, 50 °C, 24 h.

external surface of the MOF particles. Yet, the crystalline structure of Ti-MIL-125 may collapse under turnover conditions of liquid-phase oxidation [66]. We also tested catalytic activity of Ti-MIL-125 in CO_2 cycloaddition to SO. After 48 h at 25 °C and 8 bar CO_2, the yield of SC was only 13%. Previously, Srivastava et al. demonstrated that mesoporous Ti-MCM-41 was more active and selective in CO_2 cycloaddition to SO than microporous TS-1, while the catalysts showed similar activity for epoxides of smaller dimensions (e.g., epichlorohydrin or propylene oxide) [45].

We evaluated the impact of the reaction conditions (solvent nature, temperature and styrene concentration) on the styrene conversion and carbonate selectivity using Ti-MMM-E as the most prospective catalyst among the Ti-catalysts studied. The effect of solvent nature is shown in Fig. 1. Methanol was found to be the least suitable solvent in terms of both catalyst activity and selectivity (8% SC selectivity at 7% styrene conversion versus 21% selectivity at 47% conversion in MeCN), while ethylacetate, the most sought-after solvent in terms of environmental sustainability, showed 41% selectivity at a reasonable (28%) substrate conversion. As a result, SC yields in ethylacetate and MeCN after 24 h were close (11 and 10%, respectively).

Fig. 2 demonstrates the influence of the reaction temperature on styrene conversion and products distribution after 24 h in MeCN. Rise of the temperature from 30 to 70 °C increased both substrate conversion and SC selectivity. However, further increase of the temperature up to 90 °C reduced selectivity, most likely because of overoxidation and/or polymerization processes.

Finally, we attempted a multiplication of the reactants loading in the reactor to get a higher volume yield of the target product. Fig. 3 shows that increase in the initial concentration of styrene while keeping constant the molar ratio of all the reactants improved carbonate selectivity and substrate conversion, which attained 47 and 50% at 0.5 M of styrene after 24 h. The results obtained using Ti-MMM-E are comparable with the results reported by Srivastava
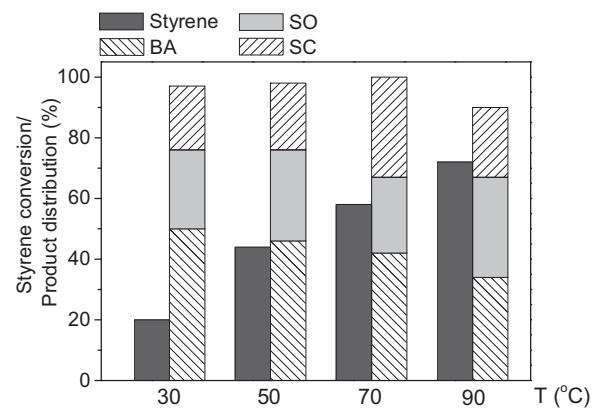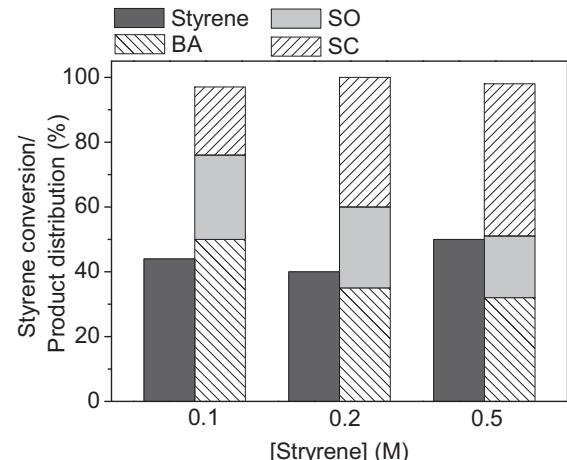
et al. for Ti-MCM-41/TBHP [45], though with Ti-MMM-E milder reaction conditions and more convenient one-step procedure were employed.

As one can see from the data collected in Table 4, rise of the initial concentration of styrene from 1.0 M up to solvent-free conditions (i.e., 2.4 M) at constant catalyst loading enhanced SC selectivity, which reached 57 and 68% at 40 and 72% conversion after 24 and 48 h at 50 °C, respectively. Increasing the reaction temperature to 70 °C under the solvent-free conditions, we attained 67 and 70% SC selectivities at styrene conversions of 67 and 92% after 24 and 48 h, respectively (Table 4, entry 4). This enabled the volume yield of SC as high as 0.3 kg per L of the reaction mixture, which is superior to the volume yield of 0.04 kg/L obtained by Srivastava et al. using Ti-MCM-41/TBHP system [45]. The isolated yield of styrene carbonate (see Section 2 for details) obtained after 48 h of reac-

Table 4
Effect of concentration and temperature on styrene oxidative carboxylation with TBHP and CO_2 over Ti-MMM-E.

Entry	[Styrene] (M)	T (°C)	Time (h)	Styrene conversion (%)	Product selectivity[a] (%)		
					BA	SO	SC
1	1.0	50	24	65	43	23	33
			48	85	39	22	39
2	1.7	50	24	37	28	17	54
3	2.4[b]	50	24	40	24	19	57
			48	72	17	15	68
4	2.4[b]	70	24	67	16	16	67
			48	92	15	10	70(59)[c]
5[d]	3.1[b]	70	24	60	17	7[e]	65
			48	82	19	9[e]	66

Reaction conditions: styrene/TBHP/TBABr molar ratio = 1/1.5/0.1, Ti-MMM-E 300 mg (0.093 mmol Ti), MeCN (if any), P(CO_2) 8 bar.
[a] GC yield based on substrate consumed.
[b] Solvent-free conditions.
[c] Selectivity based on isolated yield.
[d] 70% aqueous TBHP was used instead of 5.5 M solution in decane.
[e] 1-Phenyl-1,2-ethanediol was also formed.

Table 5
Oxidative carboxylation of various olefins by Ti-MMM-E/TBABr/TBHP/CO_2 system.

Entry	Olefin	Substrate conversion (%)	Carbonate selectivity (%)
1	Styrene	92	70
2	4-Methylstyrene	98.5	69[a]
3	4-Methoxystyrene	95	38[b]
4	4-Chlorostyrene	62	44[c]
5	Cyclohexene	68	_[d]
6	Hexene-1	19	Traces[e]

Reaction conditions: olefin 4.8 mmol, TBHP 7.2 mmol, TBABr 0.48 mmol, Ti-MMM-E 300 mg (0.093 mmol Ti), 70 °C, P(CO_2) 8 bar, 48 h.
[a] Other products: 4-methylbenzaldehyde (4%), 4-methylstyrene oxide (1%), and 4-methylbenzoic acid (26%).
[b] Other products: 4-methoxybenzaldehyde (35%), 4-methoxystyrene oxide (8%), and 4-methoxybenzoic acid (13%).
[c] Other products: 4-chlorobenzaldehyde (3%), 4-chlorostyrene oxide (5%), 4-chloroacetophenone (13%), and 4-chlorobenzoic acid (35%).
[d] Main products: 1,2-epoxycyclohexane (22%), 2-cyclohexen-1-ol (11%), 2-cyclohexen-1-one (25%), 1,2-cyclohexane diol (23%), 2-bromocyclohexanol (8%), and 1,2-dibromocyclohexane (5%).
[e] Main products: 1,2-epoxyhexane (36%), propyl vinyl ketone (36%), and 1,2-dibromohexane (22%).

tion at 70 °C was 54% (the corresponding GC yield 64%). Moreover, the reaction can be carried out using aqueous TBHP instead of its solution in decane without significant deterioration of the catalytic performance (Table 4, entry 5). In this case, involvement of any organic solvents is completely avoided. Since water is present, styrene oxide was partially converted to 1-phenyl-1,2-ethanediol; however, the yield of SC remained high. Importantly, TBABr can be separated from the carbonate product by extraction with water (see Section 2 for details). tert-Butanol that is released from TBHP in the course of the reaction can be converted into commercially valuable chemicals, e.g., dehydrated to isobutene and etherified with methanol or ethanol for the production of octane boosters [82].

To estimate the scope of the Ti-MMM-E/TBABr/TBHP/CO_2 system, we studied oxidative carboxylation of some other representative olefins under the reaction conditions that had been determined as optimal for the formation of styrene carbonate in terms of both substrate conversion and product yield (no solvent, 70 °C). The results are summarized in Table 5. While Ti-MMM-E catalyzed effectively oxidative carboxylation of 4-methylstyrene to give the corresponding carbonate with the yield of 68% (Table 5, entry 2), 4-methoxystyrene and 4-chlorostyrene appeared to be less prone to oxidative carboxylation than styrene and 4-methylstyrene (Table 5, compare entry 3 and 4 with entries 1 and 2), which is in agreement with the literature [39,83]. We have also tested the Ti-MMM-E/TBABr/TBHP/CO_2 system for the oxidative carboxylation of cyclohexene and hexene-1 (Table 5, entries 5

and 6). However, with these substrates, no carbonates were found and the main products were epoxides along with other oxidation and bromination products. The oxidative bromination of alkenes to form bromohydrins and dibromoalkanes using an oxidant and inorganic bromide salts or alkylammonium bromides was precedented [84,85].

The mechanisms of the cycloaddition of CO_2 to epoxides and alkene oxidative carboxylation in the presence of quaternary ammonium salts as cocatalysts have been addressed in the literature [18,21,33–35,40,41,73,86,87]. It was suggested that TBABr promotes epoxide ring opening, and thus, facilitates the formation of carbonate [18,21,41,86,87]. For the oxidative carboxylation, it was also proposed that Br^- can be involved in the oxidation stage [34,40,73]. Yet, the addition of CO_2 may occur through a mechanism when CO_2 inserts directly into an intermediate formed during oxygen atom transfer step [33–35,40,73]. Further kinetic and spectroscopic studies are needed to get insight into the mechanism of the alkene oxidative carboxylation over Ti-MMM-E and to clarify the role of the TBABr cocatalyst.

3.3. Catalyst stability and recyclability

The question about stability of solid catalysts is crucial for heterogeneous catalysis in liquid phase [88]. Nevertheless, to the best of our knowledge, only few examples demonstrating catalyst recyclability have been reported so far for the oxidative carboxylation of alkenes [37,40,41,44,46]. Notably, two of them dealt with homogeneous catalysts [40,41] and required rather complicated recycling procedures that involved distillation [41] or extraction [40] of the organic reagents. In the case of supported gold catalysts [37,44] and $MoO_2(acac)_2$ + TBABr system [41] utilizing multi-step protocols, both substrate conversion and carbonate selectivity slightly reduced in the second run. Recycling experiments for the Del-Ti-MWW-$N^+Bu_3Br^-$/H_2O_2 system showed a dramatic decrease of propylene conversion (from 81 to 46%) and carbonate yield (from 48 to 29%) after the first run [46]. No recyclability tests were provided for the TS-1/H_2O_2 and Ti-MCM-41/TBHP catalytic systems [45].

Ti-MMM-E was recovered from the reaction mixture after 24 h by simple filtration and then used repeatedly in seven consecutive runs under solvent-free conditions. Fig. 4 demonstrates that the styrene conversion practically did not change during six reuses, but decreased in the seventh run, while carbonate selectivity just slightly reduced after second reuse. After 7 recycles, the total volume yield of SC as high as 1.1 kg/L could be achieved.
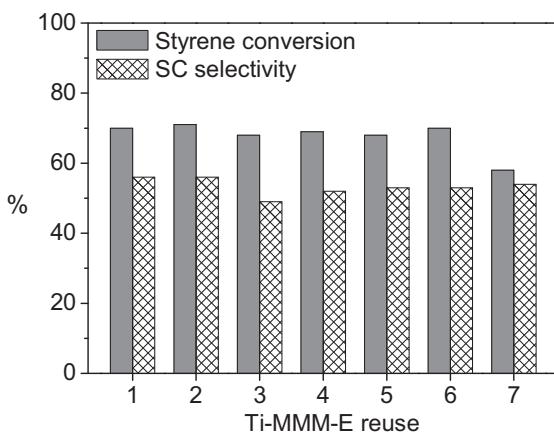
Fig. 4. Reuse of Ti-MMM-E in solvent-free styrene oxidative carboxylation. Reaction conditions as in Table 4, entry 4, 24 h.
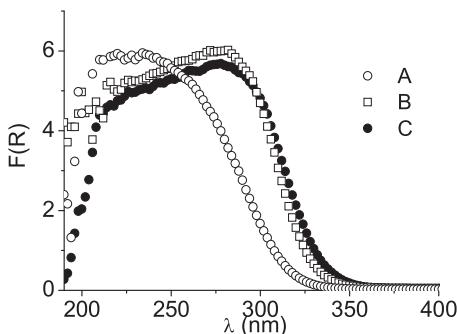
Fig. 5. DR UV–vis spectra of Ti-MMM-E: (A) initial, (B) and (C) after one and four runs of styrene oxidative carboxylation, respectively. Reaction conditions as in Table 4, entry 4, 24 h.

The N_2 adsorption measurements revealed a minor decrease in the catalyst surface area, mesopore volume and pore diameter after reuse (Table 1). The content of titanium in the catalysts remained intact after four reuses (see Table 1) and no titanium was found in the solution after separation of the catalyst from the reaction mixture, thereby indicating no leaching of the active metal. Studies by SEM indicated some reduction of the particles size and narrowing of their distribution (100–200 μm) after the catalytic runs (Fig. S2), likewise in the oxidation of 2,3,6-trimethylphenol with H_2O_2 over Ti-MMM-E [63]. DR UV spectra showed some changes in the state of Ti after the catalyst reuse (Fig. 5). The observed long-wave shift of the absorption is a manifestation of further oligomerization of titanium active species on the catalyst surface, the process typical of titanium-silicate catalysts in liquid-phase oxidations [54,89,90]. Similarly, a gradual aggregation of Ti centers into ultrafine titania clusters under operation conditions has been established for the Shell epoxidation catalyst [90].

4. Conclusions

The mesoporous titanium-silicate Ti-MMM-E prepared by the simple and affordable evaporation-induced self-assembly methodology demonstrated superior catalytic performance in terms of substrate conversion and carbonate selectivity in the one-step oxidative carboxylation of styrene and 4-methylstyrene with the environmentally benign oxidant, TBHP, in the presence of tetrabutylammonium bromide cocatalyst under mild solvent-free conditions (50–70 °C, 8 bar CO_2). The selectivity towards styrene and 4-methylstyrene carbonates reached ca. 70% at 92 and 98.5% substrate conversion, respectively. Importantly, no leaching of the active metal into solution occurred and the Ti-MMM-E catalyst could be easily recycled and reused with maintenance of the catalytic properties under solvent-free conditions. The volume yield of styrene carbonate as high as 1.1 kg/L was achieved after seven catalyst reuses. The catalyst preserved its mesoporous structure and the state of titanium active centers. Other types of mesoporous and microporous Ti-containing catalysts, including the metal-organic framework MIL-125, were less active and selective. Detailed kinetic and spectroscopic studies would shed light on the mechanism of the oxidative carboxylation over Ti-MMM-E and elucidate the role of the TBABr cocatalyst.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.apcatb.2015.08.010

References

[1] R. Zevenhoven, S. Eloneva, S. Teir, Catal. Today 115 (2006) 73–79.
[2] T. Sakakura, J. Choi, H. Yasuda, Chem. Rev. 107 (2007) 2365–2387.
[3] M. Aresta, A. Dibenedetto, Dalton Trans. (2007) 2975–2992.
[4] L.N. He, J.Q. Wang, J.L. Wang, Pure Appl. Chem. 81 (2009) 2069–2080.
[5] T. Sakakura, K. Kohno, Chem. Commun. (2009) 1312–1330.
[6] J. Ma, N. Sun, X. Zhang, N. Zhao, F. Xiao, W. Wei, Y. Sun, Catal. Today 148 (2009) 221–231.
[7] M. Aresta (Ed.), Carbon Dioxide as Chemical Feedstock, Wiley-VCH, Weinheim, 2010.
[8] D.J. Darensbourg, Inorg. Chem. 49 (2010) 10765–10780.
[9] I. Omae, Coord. Chem. Rev. 256 (2012) 1384–1405.
[10] A.M. Appel, J.E. Bercaw, A.B. Bocarsly, H. Dobbek, D.L. DuBois, M. Dupuis, J.G. Ferry, E. Fujita, R. Hille, P.J.A. Kenis, C.A. Kerfeld, R.H. Morris, C.H.F. Peden, A.R. Portis, S.W. Ragsdale, T.B. Rauchfuss, J.N.H. Reek, L.C. Seefeldt, R.K. Thauer, G.L. Waldrop, Chem. Rev. 113 (2013) 6621–6658.
[11] C. Maeda, Y. Miyazaki, T. Ema, Catal. Sci. Technol. 4 (2014) 1482–1497.
[12] M.M. Halmann, M. Steinberg, Greenhouse Gas Carbon Dioxide Mitigation: Science and Technology, Lewis Publishers, Boca Raton, Florida, 1999.
[13] D. Bakker, A. Watson, Nature 410 (2001) 765–766.
[14] C. Song, Catal. Today 115 (2006) 2–32.
[15] S. Fukuoka, M. Kawamura, K. Komiya, M. Tojo, H. Hachiya, K. Hasegawa, M. Aminaka, H. Okamoto, I. Fukawa, S. Konno, Green Chem. 5 (2003) 497–507.
[16] G.W. Coates, D.R. Moore, Angew. Chem. Int. Ed. 43 (2004) 6618–6639.
[17] W.-L. Dai, S.-L. Luo, S.-F. Yin, C.-T. Au, Appl. Catal. A: Gen. 366 (2009) 2–12.
[18] M. North, R. Pasquale, C. Young, Green Chem. 12 (2010) 1514–1539.
[19] M.R. Kember, A. Buchard, C.K. Williams, Chem. Commun. 47 (2011) 141–163.
[20] D.J. Darensbourg, S.J. Wilson, Green Chem. 14 (2012) 2665–2671.
[21] P.P. Pescarmona, M. Taherimehr, Catal. Sci. Technol. 2 (2012) 2169–2187.
[22] M. Zhu, M.A. Carreon, J. Appl. Polym. Sci. 131 (2013) 39738.
[23] J. Wang, J. Leong, Y. Zhang, Green Chem. 16 (2014) 4515–4519.
[24] B.-H. Xu, J.-Q. Wang, J. Sun, Y. Huang, J.-P. Zhang, X.-P. Zhang, S.-J. Zhang, Green Chem. 17 (2015) 108–122.
[25] C. Martín, G. Fiorani, A.W. Kleij, ACS Catal. 5 (2015) 1353–1370.
[26] J.J. McKetta, W.A. Cunningham (Eds.), Encyclopedia of Chemical Processing and Design, vol. 20, Marcel Decker, New York, 1984, p. 177.
[27] A. Behr, Angew. Chem. Int. Ed. 27 (1988) 661–678.
[28] D.C. Webster, Prog. Org. Coat. 47 (2003) 77–86.
[29] P. Ziosi, T. Tabanelli, G. Fornasari, S. Cocchi, F. Cavani, P. Righi, Catal. Sci. Technol. 4 (2014) 4386–4395.
[30] U.S. Patent 3025305, 1962.
[31] M. Aresta, E. Quaranta, J. Mol. Catal. 41 (1987) 355–359.
[32] M. Aresta, A. Dibenedetto, I. Tommasi, Appl. Organomet. Chem. 14 (2000) 799–802.
[33] D. Bai, H. Jing, Green Chem. 12 (2010) 39–41.

[34] J.M. Sun, S. Fujita, B.M. Bhanage, M. Arai, Catal. Today 93–95 (2004) 383–388.
[35] J.M. Sun, S. Fujita, B.M. Bhanage, M. Arai, Catal. Commun. 5 (2004) 83–87.
[36] O.V. Zalomaeva, N.V. Maksimchuk, A.M. Chibiryaev, K.A. Kovalenko, V.P. Fedin, B.S. Balzhinimaev, J. Energy Chem. 22 (2013) 130–135.
[37] J. Sun, S. Fujita, F. Zhao, M. Hasegawa, M. Arai, J. Catal. 230 (2005) 398–405.
[38] Y. Wang, J. Sun, D. Xiang, L. Wang, J. Sun, F.-S. Xiao, Catal. Lett. 129 (2009) 437–443.
[39] N. Eghbali, C.J. Li, Green Chem. 9 (2007) 213–215.
[40] J.-L. Wang, J.-Q. Wang, L.-N. He, X.-Y. Dou, F. Wu, Green Chem. 10 (2008) 1218–1223.
[41] F. Chen, T. Dong, T. Xu, X. Li, C. Hu, Green Chem. 13 (2011) 2518–2524.
[42] F. Ono, K. Qiao, D. Tomida, C. Yokoyama, Appl. Catal. A: Gen. 333 (2007) 107–113.
[43] A.-L. Girard, N. Simon, M. Zanatta, S. Marmitt, P. Gonçalves, J. Dupont, Green Chem. 16 (2014) 2815–2825.
[44] D. Xiang, X. Liu, J. Sun, F.-S. Xiao, J. Sun, Catal. Today 148 (2009) 383–388.
[45] R. Srivastava, D. Srinivas, P. Ratnasamy, Catal. Lett. 91 (2003) 133–139.
[46] J. Zhang, Y. Liu, N. Li, H. Wu, X. Li, W. Xie, Z. Zhao, P. Wu, M. He, Chin. J. Catal. 29 (2008) 589–591.
[47] T. Maschmeyer, F. Rey, G. Sankar, J.M. Thomas, Nature 378 (1995) 159–162.
[48] A. Corma, Chem. Rev. 97 (1997) 2373–2420.
[49] A. Notari, Adv. Catal. 41 (1996) 253–334.
[50] R.J. Saxton, Topics Catal. 9 (1999) 43–57.
[51] C. Perego, A. Carati, P. Ingalina, M.A. Mantegazza, G. Bellussi, Appl. Catal. A: Gen. 221 (2001) 63–72.
[52] P. Ratnasamy, D. Srinivas, H. Knozinger, Adv. Catal. 48 (2004) 1–169.
[53] M.G. Clerici, M.E. Dómine, in: M.G. Clerici, O.A. Kholdeeva (Eds.), Liquid Phase Oxidation via Heterogeneous Catalysis, Wiley, New Jersey, 2013, pp. 21–93 (Chapter 2).
[54] O.A. Kholdeeva, in: M.G. Clerici, O.A. Kholdeeva (Eds.), Liquid Phase Oxidation via Heterogeneous Catalysis, Wiley, New Jersey, 2013, pp. 127–219 (Chapter 4).
[55] R. Hutter, T. Mallat, A. Baiker, J. Catal. 153 (1995) 177–189.
[56] A. Corma, M. Domine, J.A. Gaona, J.L. Jorda, M.T. Navarro, F. Rey, J. Perez-Pariente, J. Tsuji, B. McCulloch, L.T. Neneth, Chem. Commun. (1998) 2211–2212.
[57] J.M. Fraile, J.I. Garcia, J.A. Mayoral, E. Vispe, J. Catal. 189 (2000) 40–51.
[58] A. Bhaumik, T. Tatsumi, J. Catal. 189 (2000) 31–39.
[59] Z. Shan, J.C. Jansen, L. Marchese, T. Maschmeyer, Micropor. Mesopor. Mater. 48 (2001) 181–187.
[60] M. Guidotti, L. Conti, A. Fusi, N. Ravasio, R. Psaro, J. Mol. Catal. A: Chem. 182–183 (2002) 151–156.
[61] J.M. Fraile, J.I. García, J.A. Mayoral, E. Vispe, J. Catal. 233 (2005) 90–99.
[62] M. Guidotti, N. Ravasio, R. Psaro, E. Gianotti, S. Coluccia, L. Marchese, J. Mol. Catal. A: Chem. 250 (2006) 218–225.
[63] I.D. Ivanchikova, M.K. Kovalev, M.S. Mel'gunov, A.N. Shmakov, O.A. Kholdeeva, Catal. Sci. Technol. 4 (2014) 200–207.
[64] O.A. Kholdeeva, M.S. Melgunov, A.N. Shmakov, N.N. Trukhan, V.V. Kriventsov, V.I. Zaikovskii, M.E. Malyshev, V.N. Romannikov, Catal. Today 91–92 (2004) 205–209.
[65] M. Dan-Hardi, C. Serre, T. Frot, L. Rozes, G. Maurin, C. Sanchez, G. Férey, J. Am. Chem. Soc. 131 (2009) 10857–10859.
[66] I.D. Ivanchikova, J.-S. Lee, N.V. Maksimchuk, A.N. Shmakov, Y.A. Chesalov, A.B. Ayupov, Y.K. Hwang, C.-H. Jun, J.-S. Chang, O.A. Kholdeeva, Eur. J. Inorg. Chem. (2014) 132–139.
[67] Y.-M. Shen, W.-L. Duan, M. Shi, Adv. Synth. Catal. 345 (2003) 337–340.
[68] J.-W. Huang, M. Shi, J. Org. Chem. 68 (2003) 6705–6709.
[69] A. Tuel, L.G. Hubert-Pfalzgraf, J. Catal. 217 (2003) 343–353.
[70] L. Marchese, T. Maschmeyer, E. Gianotti, S. Coluccia, J.M. Thomas, J. Phys. Chem. B 101 (1997) 8836–8838.
[71] B.J. Aronson, C.F. Blanford, A. Stein, Chem. Mater. 9 (1997) 2842–2851.
[72] X. Gao, I.E. Wachs, Catal. Today 51 (1999) 233–254.
[73] J. Sun, S. Fujita, M. Arai, J. Organometall. Chem. 690 (2005) 3490–3497.
[74] F.-S. Xiao, Y. Han, Y. Yu, X. Meng, M. Yang, S. Wu, J. Am. Chem. Soc. 9 (2002) 888–889.
[75] V. Hulea, E. Dumitriu, Appl. Catal. A 277 (2004) 99–106.
[76] X. Wang, X. Zhang, Y. Wang, H. Liu, J. Qiu, J. Wang, W. Han, K.L. Yeung, ACS Catal. 1 (2011) 437–445.
[77] J. Wang, J. Lu, J. Yang, R. Chen, Y. Zhang, D. Yin, J. Wang, Appl. Surf. Sci. 283 (2013) 794–801.
[78] J.M. Fraile, N. García, J.A. Mayoral, F.G. Santomauro, M. Guidotti, ACS Catal. 5 (2015) 3552–3561.
[79] A. Dhakshinamoorthy, M. Alvaro, H. Garcia, ACS Catal. 1 (2011) 836–840.
[80] M.A. Uguina, D.P. Serrano, R. Sanz, J.L.G. Fierro, M. López-Granados, R. Mariscal, Catal. Today 61 (2000) 263–270.
[81] S.-N. Kim, J. Kim, H.-Y. Kim, H.-Y. Cho, W.-S. Ahn, Catal. Today 204 (2013) 85–93.
[82] G. Strukul, A. Scarso, in: M.G. Clerici, O.A. Kholdeeva (Eds.), Liquid Phase Oxidation via Heterogeneous Catalysis, Wiley, New Jersey, 2013, pp. 1–20 (Chapter 2).
[83] X. Yang, J. Wu, X. Mao, T.F. Jamison, T.A. Hatton, Chem. Commun. 50 (2014) 3245–3248.
[84] A. Podgoršek, M. Zupan, J. Iskra, Angew. Chem. Int. Ed. 48 (2009) 8424–8450.
[85] K. Yonehara, K. Kamata, K. Yamaguchi, N. Mizuno, Chem. Commun. 47 (2011) 1692–1694.
[86] J.-Q. Wang, K. Dong, W.-G. Cheng, J. Sun, S.-J. Zhang, Catal. Sci. Technol. 2 (2012) 1480–1484.
[87] Y. Yang, Y. Hayashi, Y. Fujii, T. Nagano, Y. Kita, T. Ohshima, J. Okuda, K. Mashima, Catal. Sci. Technol. 2 (2012) 509–513.
[88] R.A. Sheldon, M. Wallau, I.W.C.E. Arends, U. Schuchardt, Acc. Chem. Res. 31 (1998) 485–493.
[89] O.A. Kholdeeva, Catal. Sci. Technol. 4 (2014) 1869–1889.
[90] J.K.F. Buijink, J.-P. Lange, A.N.R. Bos, A.D. Horton, F.G.M. Niele, in: S.T. Oyama (Ed.), Mechanisms in Homogeneous and Heterogeneous Epoxidation Catalysis, Elsevier, Amsterdam, 2008, pp. 356–371.